Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Studies in Batch and Continuous Solvent Sublation. II. Continuous Countercurrent Solvent Sublation of Neutral and Ionic Species from Aqueous Solutions

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To cite this Article Valsaraj, K. T. and Thibodeaux, L. J.(1991) 'Studies in Batch and Continuous Solvent Sublation. II. Continuous Countercurrent Solvent Sublation of Neutral and Ionic Species from Aqueous Solutions', Separation Science and Technology, 26: 3, 367 — 380

To link to this Article: DOI: 10.1080/01496399108050478

URL: http://dx.doi.org/10.1080/01496399108050478

SEPARATION SCIENCE AND TECHNOLOGY, 26(3), pp. 367–380, 1991

Studies in Batch and Continuous Solvent Sublation. II. Continuous Countercurrent Solvent Sublation of Neutral and Ionic Species from Aqueous Solutions

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Abstract

A complete mathematical model is proposed for the continuous countercurrent operation of a solvent sublation column. It takes into account all possible transport mechanisms in sublation. This is an extension of a previously published model for a lab-scale batch process. Experimental results on the continuous countercurrent removal of pentachlorophenol as a pentachlorophenolate + hexadecyltrimethyl ammonium bromide complex into decyl alcohol is also reported and checked against the model.

INTRODUCTION

A number of recent publications have shown that solvent sublation is a useful technique for the removal of a variety of neutral hydrophobic compounds (both volatile and nonvolatile) from aqueous solutions (*1–6*). It is also a useful method for the removal of hydrophilic ionic compounds that can be converted to hydrophobic ion–surfactant complexes (*1, 5*). Most of the work to date has been on a semibatch scale, i.e., air in a once-pass-through mode with stagnant aqueous and organic solvent phases. Such a mode of operation is very useful in understanding the basic mechanisms of transport of compounds in a solvent sublation process (*1*). However, it is of little value as far as scale up to large scale processes is concerned. Figure 1 shows the various modes of operations possible for solvent sublation. In the present paper we report our experiments where the aqueous phase is in a continuous countercurrent mode. The organic phase is main-

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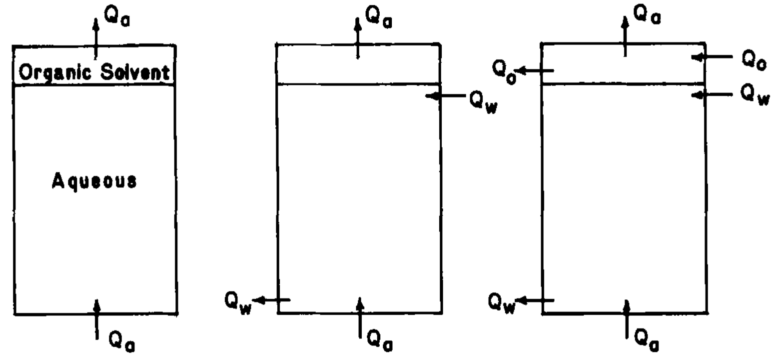
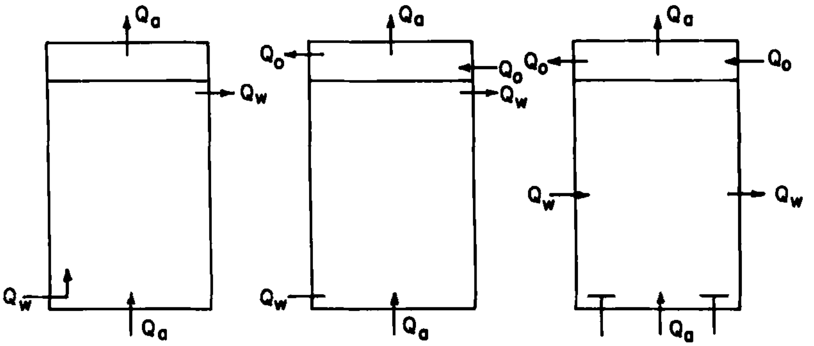


(a)
Semi-Batch
Aq. Phase Stagnant
Org. Phase Stagnant

(b)
Aq. Phase Continuous
Countercurrent
Org. Phase Stagnant

(c)
Aq. and Org. Phases
Continuous
Countercurrent



(d)
Aq. Phase Continuous
Co-current,
Org. Phase Stagnant

(e)
Aq. Phase Continuous
Co-current, Org. Phase
Continuous Co-current

(f)
Aq. Phase and
Org. Phase in
Continuous Crossflow

FIG. 1. Various possible modes of operation of a solvent sublation column.

tained as a stagnant layer. Many of the earlier reports on solvent sublation in the semibatch mode have shown that in order for the process to be successful, air bubble sizes have to be kept as small as possible, even at higher air flow rates. Thus, when the process is made continuous countercurrent, one should expect severe limitations in the ratio of air to liquid flow rates that are possible. Thus, one important objective of our work is to obtain some ideas about the above aspect. We first describe a mathematical model for the countercurrent process by expanding upon our previous model for a semibatch process. Experimental results and model simulations are described subsequently.

MATHEMATICAL MODEL

In our previous work we described a complete mathematical model for a semibatch process which incorporated all known transport processes in solvent sublation (*1*). We observed that semibatch processes involving relatively small aqueous volumes could be described satisfactorily by considering the aqueous section as completely mixed where the air bubble is assumed to be in equilibrium with the aqueous phase as it exits the aqueous section. For a continuous flow process, one should discard the assumption of a completely mixed aqueous section since a discernible concentration gradient could be observed (*11*) in the aqueous phase. The use of an incompletely mixed aqueous section means the process will have to be modeled either as a dispersion flow model or as a series of interconnected stirred tanks as described by Levenspiel (*7*). It was shown by Smith that for most of the experimental conditions the two approaches are equivalent when the number of stirred tanks used is 5 or more (*8*). We felt that the stirred-tank-in-series approach would be an appropriate and convenient way to model sublation columns. A similar approach was used by Herbst and coworkers to model flotation columns (*9*). This involves the mathematical partitioning of the aqueous section into a number of slabs of equal volumes, each one completely mixed (Fig. 2). The thin, organic solvent layer is considered to be a single, well-mixed section. These considerations also necessitate discarding the assumption that the air bubble is in equilibrium with the aqueous phase. The residence time for an air bubble in each individual slab is small, and hence it is likely that the transfer of solute to the air bubble is mass transfer controlled. A preliminary discussion of such a model was described by us in a previous work (*1*).

We assume that the equilibrium relationship between the solute in the air phase inside the bubble and the aqueous phase is given by Henry's law:

$$H_c = \frac{C_v^{\text{eq}}}{C_w^{\text{eq}}} = \frac{(\text{mol/cm}^3\text{ air})}{(\text{mol/cm}^3\text{ water})} \tag{1}$$

The equilibrium relationship for the solute between the adsorbed state on the air bubble surface and the aqueous phase is given by a linear adsorption isotherm:

$$K_a = \frac{\Gamma^{\text{eq}}}{C_w^{\text{eq}}} = \frac{(\text{mol/cm}^2\text{ surface})}{(\text{mol/cm}^3\text{ water})} \tag{2}$$

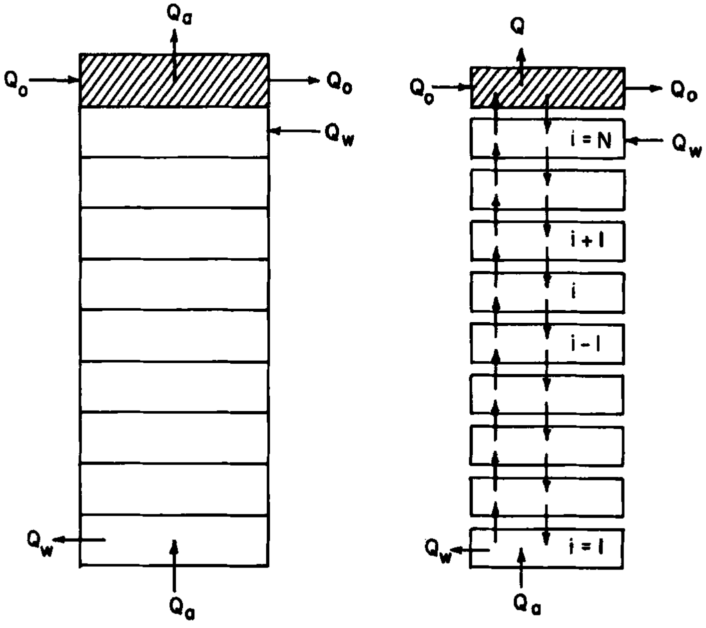


FIG. 2. Stirred-tanks-in-series model for countercurrent solvent sublation.

The solute mass transfer to the air bubble is assumed to be controlled by diffusion across a thin boundary layer around the air bubble due to a molar concentration gradient, $C_w - C_w^{eq}$, where C_w is the actual concentration in the aqueous phase and C_w^{eq} is the concentration at the air bubble/water interface at equilibrium. It is also assumed that solute mass transfer to the vapor phase inside the air bubble and to the surface adsorbed phase of the bubble occur simultaneously and parallel, so that the two mechanisms are concerted processes. We have

$$\begin{aligned} m &= 4\pi a^2 \Gamma^{eq} + \frac{4}{3}\pi a^3 C_v^{eq} \\ &= 4\pi a^2 \left(K_a + \frac{a}{3} H_c \right) C_w^{eq} \end{aligned} \tag{3}$$

Thus

$$dm/dt = 4\pi a^2 k_w [C_w - C_w^{eq}] \tag{4}$$

Using Eq. (3) in Eq. (4) and rearranging, we obtain

$$\frac{dm}{dt} + \alpha m = \beta C_w \tag{5}$$

where

$$\alpha = \frac{k_w}{\left(K_a + \frac{a}{3}H_c\right)} \quad \text{and} \quad \beta = 4\pi a^2 k_w$$

We can now use the approximation that during the very short residence time of a bubble ($\tau = h/u$, where u is the rise velocity of the bubble and h is the height of the aqueous slab), the overall aqueous concentration, C_w, does not change significantly, and then obtain (*10*, *11*)

$$m(\tau) = m(0)e^{-\alpha\tau} + \frac{\beta}{\alpha}(1 - e^{-\alpha\tau})C_w \tag{6}$$

If $N = 1$, then $m(0) = 0$. This equation holds for any slab with $m(\tau) = m_i$ and $m(0) = m_{i-1}$, so that

$$m_i = m_{i-1}e^{-\alpha\tau_i} + \frac{\beta}{\alpha}C_i(1 - e^{-\alpha\tau_i}) \tag{7}$$

where C_i is the solute concentration in the ith aqueous slab and τ_i is the rise time of an air bubble in the ith slab. The rate of change in solute concentration in any stirred tank i is given by

$$V_i\frac{dC_i}{dt} = -\frac{Q_a}{v_{bi}}(m_i - m_{i-1}) + Q_w(C_{i+1} - C_i) \tag{8}$$

where v_{bi} is the volume of an air bubble in the ith slab, Q_a is the air flow rate, and Q_w is the influent feed rate. Equation (8) has to be appropriately modified for slabs $i = 1$ and $i = N$. For $i = 1$, we have

$$V_1\frac{dC_1}{dt} = -\frac{Q_a}{v_{b1}}m_1 + Q_w(C_2 - C_1) \tag{9}$$

For $i = N$, we need to include terms resulting from solute transport due to molecular diffusion between the organic and aqueous phases driven by a solute concentration gradient, $(C_N - C_o/K_{ow})$, where K_{ow} is the solute partition constant between the organic and aqueous phases. Air bubbles at the top of the aqueous slab N coalesce to become larger, then overcome the interfacial tension and rise through the solvent phase, dragging with it a layer of water of thickness d_w. Solute is carried up along with the water. The returning water droplets have a much smaller concentration of solute. It appears fair to assume equilibrium for the returning water droplets with the organic solvent. Ultimately this process of solute being dragged up with the water and of solute returning to the top aqueous slab with the draining water would reach a study state. Including all these processes, we have for slab $i = N$:

$$V_N\frac{dC_N}{dt} = \frac{-Q_a}{v_{bN}}(m_N - m_{N-1}) + Q_w(C_{\text{infl}} - C_N) - \pi r_c^2 k_l\left(C_N - \frac{C_o}{K_{ow}}\right) - Q_a\frac{3}{a_o}d_w\left[C_N - \frac{C_o}{K_{ow}}\right] \quad (10)$$

The organic solvent layer can be considered a single, well-mixed layer due both to its very small volume and to the long bubble residence time (slow rise velocity) which give rise to an equilibrium condition for the bubble. An overall solute mass balance in the solvent layer should also include the possible transport of material to the atmosphere within air bubbles.

The differential equation for the solute in the organic layer is

$$V_o\frac{dC_o}{dt} = \frac{Q_a}{v_{bN}}(m_N) + \pi r_c^2 k_l\left(C_N - \frac{C_o}{K_{ow}}\right) - Q_oC_o - Q_a d_w\frac{3}{a_o}\left(\frac{C_o}{K_{ow}} - C_N\right) - Q_a\frac{H_c}{K_{ow}}C_o \quad (11)$$

where for the sake of complete generality of the model we have considered a continuous replenishment of the solvent layer also at a flow rate Q_o. Equations (7)–(11) are then integrated forward in time by using a simple predictor-corrector method (*10*) and knowing the initial solute concentrations in the aqueous and organic solvent layers. The model is general enough to consider even sudden upsets in air flow and influent feed rates so that a dynamic model also useful in understanding process control operations is available.

For tall, narrow bubble columns such as the ones used in solvent sublation and column flotation operations, the radii of the air bubbles change considerably as they rise through the aqueous section due to the decrease in hydrostatic pressure with increasing column height. This means both bubble radius and rise velocity have to be corrected at every point along the column height. The bubble radius in any slab i is given by

$$a_i = a_b\left(\frac{3v_{bi}}{4\pi a_b^3}\right)^{1/2} \tag{12}$$

where a_b is the bubble radius at 1 atm pressure and v_{bi} is given by

$$v_{bi} = \frac{4}{3}\pi a_b^3\left[\frac{1033.2}{1033.2 + \rho_w h_i(N + 0.5 - i)}\right] \tag{13}$$

where ρ_w is the aqueous phase density, h_i is the height of the ith slab, and N represents the total number of mixed stages in the aqueous phase.

The equations described can be shown to be easily reduced to those for a semibatch process involving small aqueous depths by assuming a completely mixed aqueous section and equilibrium for the bubble with the aqueous phase throughout the column. The final equations are described in our previous work (*1*).

EXPERIMENTAL

The experimental apparatus used was described previously (*1*) as was the procedure for both semibatch and continuous countercurrent solvent sublation. The compounds removed were neutral pentachlorophenol (PCP) into mineral oil at pH = 3.0, neutral PCP into decyl alcohol at pH = 3.0, and pentachlorophenolate ion as the complex pentachlorophenolate + hexadecyltrimethyl ammonium bomide (PCP + HTMAB) into decyl alcohol at pH = 8.9. The removals of PCP as both neutral species below its pK_a of 4.7 and as ionic species above its pK_a were studied in a countercurrent mode and are reported in the present work. The analysis of PCP in the influent and effluent were accomplished by using a UV spectrophotometer (Hewlett-Packard model 8452A) after acidification with 1 N sulfuric acid and monitoring the absorbance maximum at 214 nm. Concentrations of PCP were determined by comparison with standard solutions.

In all experiments reported in this work, the solvent phase was kept stagnant, and hence the operation was as shown in Fig. 1(b).

RESULTS AND DISCUSSION

In the first of our series of papers on solvent sublation (*1*), we described the model for a semibatch process by considering the bubble to always be in equilibrium with the aqueous phase surrounding it. In the present model, as already mentioned, this assumption was relaxed. Figure 3 gives the efficiencies simulated for a semibatch sublation of PCP into decyl alcohol at pH = 3.0 for various rates of mass transfer of PCP at the air–bubble–water interface. It can be seen that the removal efficiencies increase with the increasing aqueous phase mass transfer coefficient to the bubble (k_w). The efficiencies for $k_w \geq 3 \times 10^{-2}$ cm/min are equivalent to those for the results for infinite mass transfer coefficient model described earlier (*1*). Estimates of aqueous phase mass transfer coefficients using available literature correlations (*10*, *12*, *13*), as shown in Fig. 4, show that k_w for PCP ranges from 0.12 to 1.2 cm/min for air bubbles of radii 0.02 to 0.10 cm, thus showing that most bubbles are in equilibrium with the aqueous phase. Thus it seems reasonable to assume large or infinite mass transfer in our models. Figures 5–7 are simulations of single-stage batch solvent sublation and solvent extraction of neutral pentachlorophenol (pH = 3.0) into two solvents (mineral oil and decyl alcohol) and the molecular complex pen-

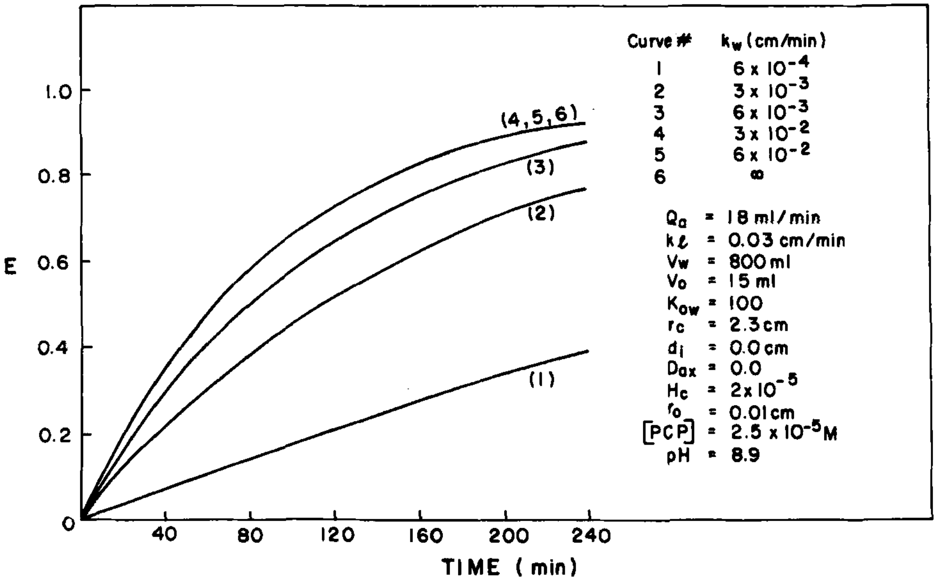


FIG. 3. Effect of finite rate of mass transfer to the air bubble from the aqueous phase on the solvent sublation of PCP in a semibatch mode.

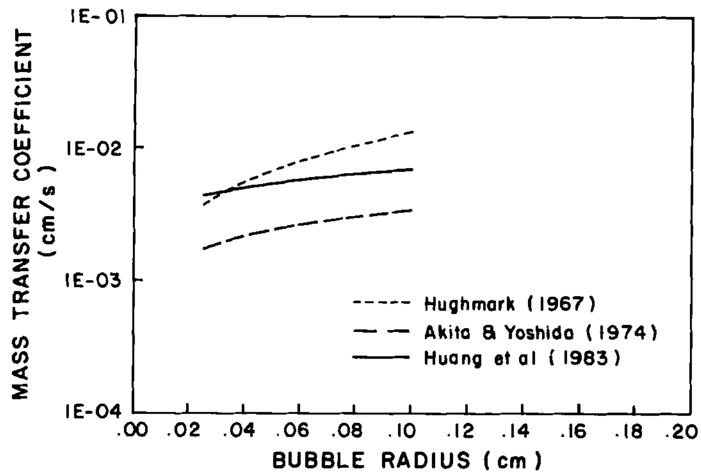


FIG. 4. Aqueous phase mass transfer coefficients to the bubble for PCP.

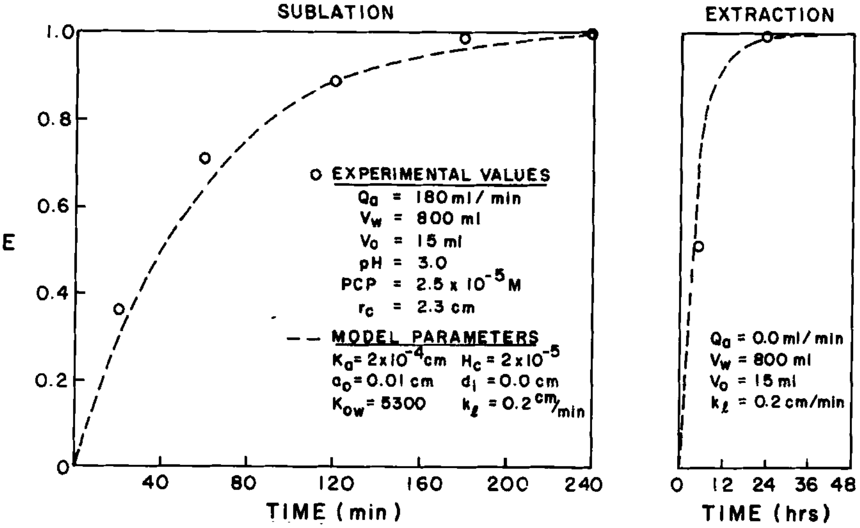


FIG. 5. Experimental efficiencies of batch solvent sublation and solvent extraction of neutral PCP into decyl alcohol at pH = 3.0. Dashed lines are model fits to experimental data (single-stage well-mixed model).

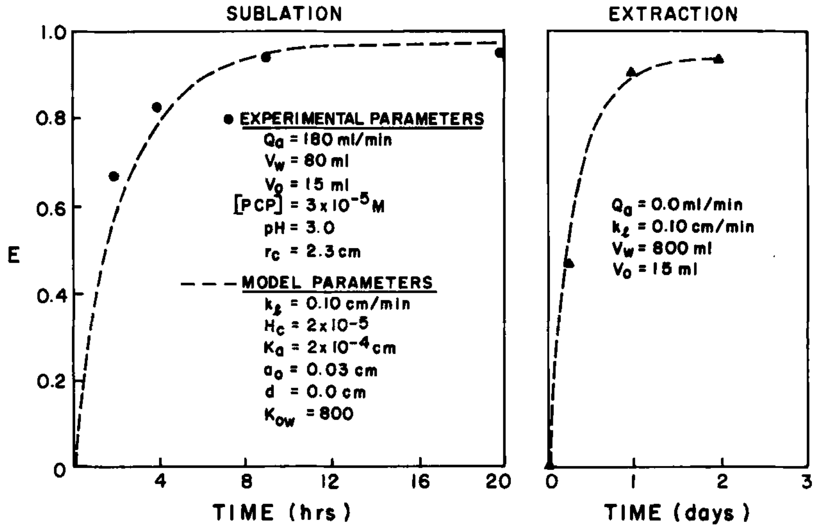


FIG. 6. Experimental efficiencies of batch solvent sublation and solvent extraction of neutral PCP into mineral oil at pH = 3.0. Dashed lines are model fits to experimental data (single-stage well-mixed model).

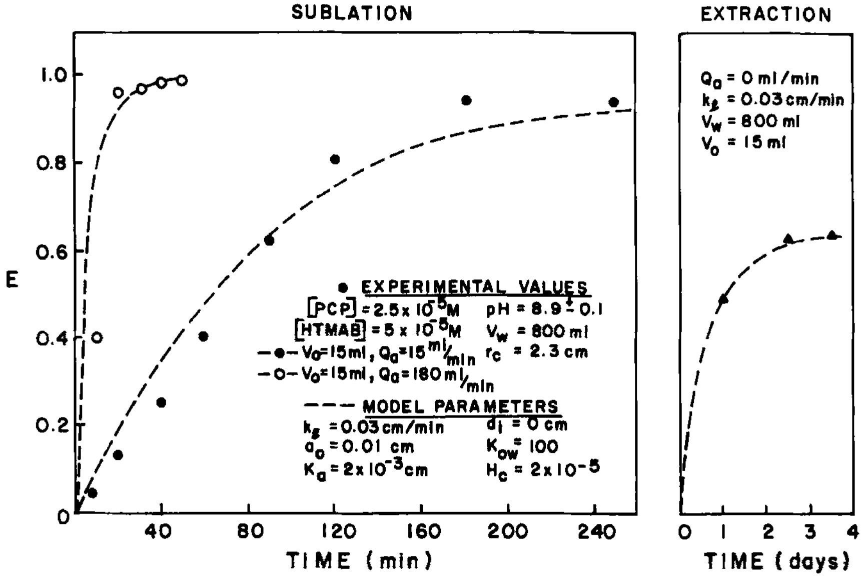
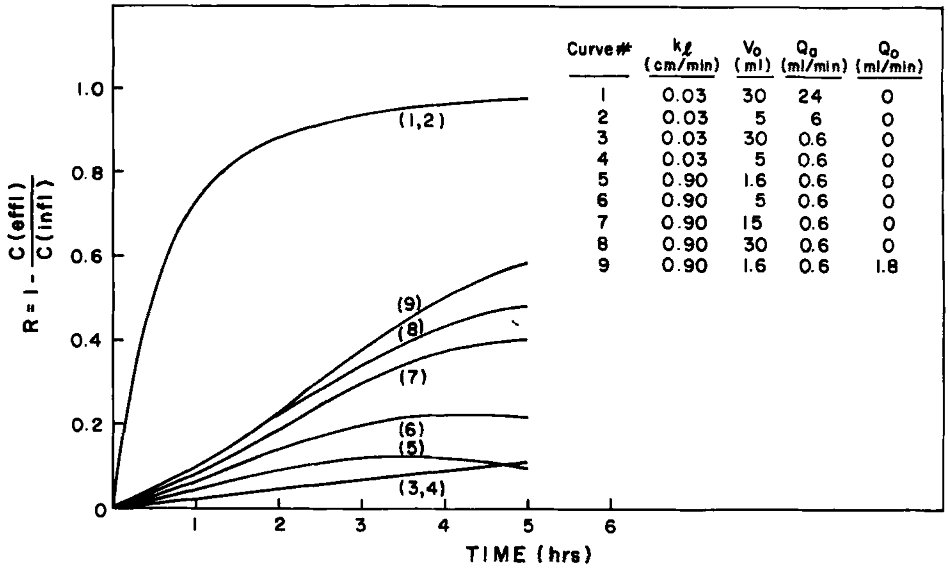


FIG. 7. Experimental efficiencies of batch solvent sublations and solvent extraction of PCP + HTMAB complex into decyl alcohol at pH = 8.9. Dashed lines are model fits to experimental data (single-stage well-mixed model).

tachlorophenolate + HTMAB (pH = 8.9) into decyl alcohol. The reasons for the choice of these solvents for specific sublations were given in our earlier paper (*1*). One of the adjustable parameters was the adsorption constant $K_a = 2 \times 10^{-3}$ cm for the PCP + HTMAB complex and $K_a = 2 \times 10^{-4}$ cm for neutral PCP. The average bubble radius used was 0.01 cm for the PCP + HTMAB complex and 0.03 cm for neutral PCP, which seem reasonable since the bubble radius in the presence of added HTMAB surfactant in the aqueous phase was observed to be smaller than in its absence. Henry's constant, H_c, was assumed to be the same ($= 2 \times 10^{-5}$) for both neutral PCP and the PCP + HTMAB complex. In reality, this means that the very small H_c value assumes that vapor-phase transport of both forms of PCP are negligible in comparison to the surface-adsorbed phase. All other parameters were experimentally obtained, including the aqueous–organic solvent partition constant, K(mineral oil–water) = 800 for neutral PCP, K(decyl alcohol–water) = 5300 for neutral PCP, and K(decly alcohol–water) = 100 for the PCP + HTMAB complex. The molecular diffusion part of the solvent sublation process is identical to that for the solvent extraction process and is given by the aqueous phase mass transfer coefficient k_l for the diffusive transport of solute across the water–solvent interface. This was the primary adjustable parameter in our model, and was it chosen as 0.2 cm/min for neutral PCP into decyl alcohol, 0.1 cm/min for neutral PCP into mineral oil, and 0.03 cm/min for the PCP + HTMAB complex into decyl alcohol. Excellent fits of model simulations to experimental data were observed.

Figure 8 shows the countercurrent model results on the effects of solvent volume, air flow rate, organic solvent replenishment rate, and effects of molecular diffusive transport across the solvent–water interface. In all these simulations, approximately 3 h or more were found necessary for steady state to be reached. A comparison of Curves 1, 2, 3, and 4 shows that as long as the molecular diffusive transport coefficient k_l is very small, the efficiency of removal with time is independent of the organic solvent volume; this is so at both high (24 mL/min) and low (0.6 mL/min) air flow rates. Curves 5, 6, 7, and 8 show that when k_l becomes larger (0.9 cm/min), the degree of removal from the aqueous phase shows a profound influence on the organic solvent volume. At low solvent volumes (v_o = 1.6 mL, Curve 5) there is a distinct maximum in removal at about 3 h into the run, which then subsequently undergoes a reduction at 4 and 5 h into the run. This is understandable since when k_l is large, the initial transfer of material by molecular diffusion is wholly in the direction of the organic solvent. When the concentration in the organic solvent reaches a large value, then the reverse transport becomes important and the degree of removal is reduced. However, when the organic solvent is not stagnant



Curve#	k_ℓ (cm/min)	V_o (ml)	Q_a (ml/min)	Q_o (ml/min)
1	0.03	30	24	0
2	0.03	5	6	0
3	0.03	30	0.6	0
4	0.03	5	0.6	0
5	0.90	1.6	0.6	0
6	0.90	5	0.6	0
7	0.90	15	0.6	0
8	0.90	30	0.6	0
9	0.90	1.6	0.6	1.8

FIG. 8. Effect of k_l, V_o, and Q_o on the continuous countercurrent solvent sublation of PCP + HTMAB complex into decyl alcohol—Model simulations. (All experimental parameters as in Fig. 7.)

but is replenished at a small rate (1.8 mL/min, Curve 9), then the degree of removal is improved considerably and the maximum no longer appears. This suggests that when k_l predominates transport, then, just as in solvent extraction in continuous solvent sublation, increased removal can be obtained by recharging the organic solvent slowly. When, however, the carry up of solute by air bubbles (through increased adsorption at the bubble–water interface) across the solvent–water interface predominates, then continuous countercurrent solvent sublation becomes independent or organic solvent volume. This is the primary advantage of solvent sublation and can be useful in concentrating a large amount of solute in a small volume of the organic solvent and thereby decontaminating a large volume of aqueous phase. The only limiting factor in this case is the maximum solubility of the solute in the organic solvent.

Figures 9 and 10 are simulations of the experimental sublation runs of the PCP + HTMAB complex at pH = 8.9 into decyl alcohol (in the countercurrent mode for the aqueous and air phases but with a stagnant decyl alcohol layer) at two different aqueous influent flow rates (5.0 and 2.5 mL/min) and at a constant air flow rate (24 mL/min). The number of mixed stages in the aqueous layer was chosen as a variable. At Q_w = 2.5

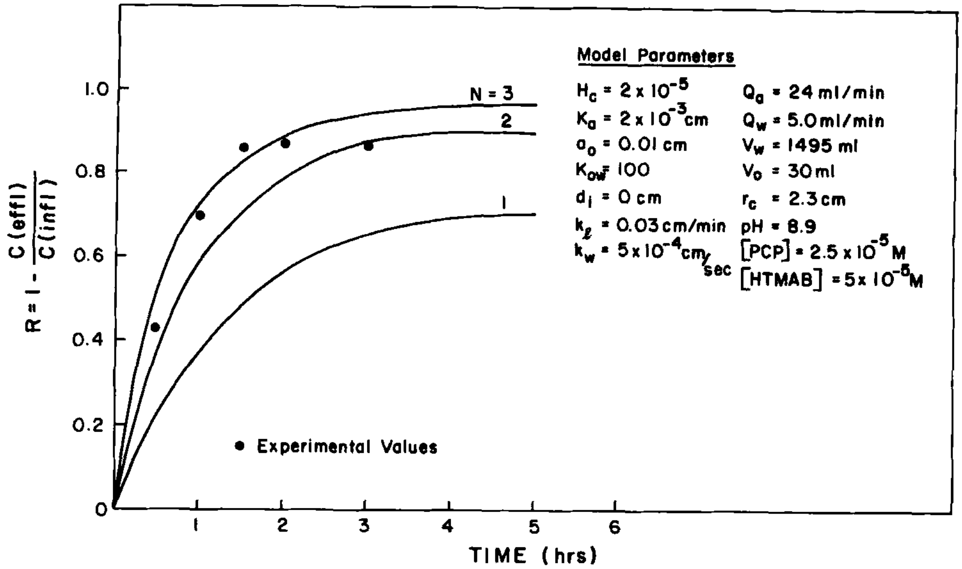


FIG. 9. Simulations of experimental results on the solvent sublation of PCP + HTMAB complex into decyl alcohol in a countercurrent mode at Q_a = 24 mL/min and Q_w = 5.0 mL/min.

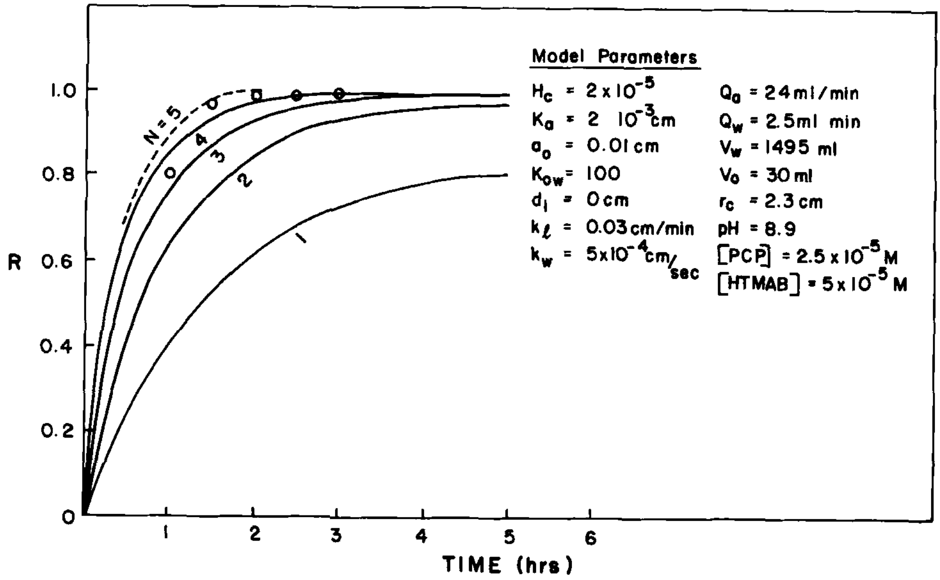


FIG. 10. Simulation of experimental results on the solvent sublation of PCP + HTMAB complex into decyl alcohol in a countercurrent mode at Q_a = 24 mL/min and Q_w = 2.5 mL/min.

mL/min, the simulation more closely resembled $N = 5$, while at Q_w = 5.0 mL/min it more closely resembled $N = 3$. This is understandable since for constant Q_a, larger Q_w values give rise to smaller concentration gradients in the aqueous phase and hence smaller steady-state removals ($R = 0.99$ at Q_w = 2.5 mL/min against $R = 0.87$ at Q_w = 5.0 mL/min). In both these simulations k_l = 0.03 cm/min, as obtained from the earlier batch scale experiments. The value of the aqueous phase mass transfer coefficient to the bubble, k_w, was chosen to be sufficiently large (5×10^{-4} cm/s) to assure equilibrium for the bubble with the aqueous phase. All other experimental parameters are given in Fig. 9. The effectiveness of continuous countercurrent solvent sublation is thus substantiated in these experiments.

Acknowledgment

This work was supported by Grant BCS-8822835 from the National Science Foundation.

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Received by editor March 8, 1990